

## ELECTROCHEMICAL SENSOR FOR SCALE BUILDING UP MEASUREMENTS

1

2

3 The present invention relates to an electrochemical  
4 sensor apparatus and method and, in particular to an  
5 electrochemical sensor that can be used to measure scale,  
6 such as mineral scale or other particulates, which  
7 deposit on the surface of pipelines or process equipment.

8

9 Mineral scale formation is one of the major flow  
10 assurance concerns in the chemical industry. The problem  
11 of scale build up arises where a fluid is flowing through  
12 a pipe or vessel and particulates precipitate out from  
13 the fluid and deposit on the surfaces of fluid-carrying  
14 equipment. This can cause a blockage to form and to the  
15 eventual failure of the equipment or disruption in the  
16 flow of the fluid.

17

18 This problem is particularly apparent in the offshore oil  
19 and gas industry. If the formation of scale or other  
20 particulate masses goes uncontrolled, the operational  
21 safety of the process or plant equipment can be  
22 compromised through the failure of subsea safety and flow  
23 control valves or other process equipment. If, for

1 example, a large mass of mineral scale forms in the riser  
2 from an oil well, the mass of scale will cause the riser  
3 to be blocked, consequently the flow of oil well fluids  
4 will be impeded and the pressure will greatly increase,  
5 thereby causing the riser to break.

6  
7 In view of this problem, it is desirable to be able to  
8 measure the amount of scale that has formed within a  
9 conduit or vessel, and also to be able to estimate and  
10 monitor the changes of likelihood that a fluid will  
11 precipitate out scale or other particulates. A  
12 measurement of the surface deposition on control surfaces  
13 or changes of scaling tendency will alert the operator to  
14 a build-up of scale. Hence, the operator of the well or  
15 chemical process will be able to treat the fluid in order  
16 to prevent scaling.

17  
18 Current methods for monitoring the extent of surface  
19 scaling and the scaling tendency in reservoirs or pipes  
20 have limitations. They tend to involve measuring water  
21 or other fluid samples, or to involve the measurement of  
22 flow variables such as pressure. These methods do not  
23 allow the operator to predict whether scaling will occur.  
24 Scale detection often comes too late using this type of  
25 monitoring, typically after a decrease in production. In  
26 general, efforts to control the scaling problem have  
27 concentrated upon strategies to mechanically or  
28 chemically remove scale.

29  
30 It is an object of the present invention to develop an  
31 electrochemical sensor that allows the operator to  
32 measure the extent of scale formation on a surface and to  
33 assess the scaling tendency of a fluid.

1

2 In accordance with a first aspect of the present  
3 invention, there is provided an electrochemical sensor  
4 comprising:

5 an electrochemical cell having a sensor means;  
6 fluid flow control means positioned so as to release a  
7 fluid jet onto the sensor means, the fluid flow control  
8 means having means for controlling the velocity of the  
9 fluid jet, the fluid flow velocity being defined by the  
10 Reynolds number of the fluid when the fluid is in the  
11 fluid flow control means; and  
12 wherein control of the Reynolds number and measurement of  
13 the electrical output of the sensor provide a measure of  
14 the build-up of scale on the working electrode.

15

16 Preferably, the measure of scale build up quantifies the  
17 scale build up on the sensor surface in the  
18 electrochemical cell.

19

20 Preferably, the sensor detects scale build up to measure  
21 the scaling tendency of the fluid.

22

23 Preferably, the fluid control means is a conduit provided  
24 with a control valve or pump.

25

26 Preferably, the sensor measures the change in electrical  
27 output as a function of Reynolds Number during use of the  
28 fluid flow control means

29

30 Preferably, the electrical output measurement means  
31 measures the limiting current response of the sensor as a  
32 function of Reynolds Number.

33

1 Preferably, the fluid flow control means is a conduit  
2 having a predefined diameter (d) and is positioned at a  
3 height (H) above the sensor having a radius (r).

4

5 Preferably, laminar flow of the fluid from the fluid  
6 control means is provided by setting said diameter (d),  
7 height (H) and radius (r).

8

9 Preferably,  $H/d = 1$ ; and  $r/d < 0.5$ .

10

11 Preferably, the apparatus of the present invention  
12 further comprises fluid sampling means for obtaining a  
13 sample of a test fluid.

14

15 Preferably, the fluid sampling means contains fluid  
16 isolation means for isolating the test fluid from a bulk  
17 fluid.

18

19 Preferably, the test fluid isolation means is provided by  
20 a container having at least one sealable valve which,  
21 when opened, allows the test fluid to enter the sampling  
22 means.

23

24 Preferably, the fluid flow control means comprises a flow  
25 meter or flow sensor for measuring flow, connected to a  
26 conduit from which said fluid jet is expelled.

27

28 Preferably, the sensor comprises a working electrode, a  
29 counting electrode and a reference electrode.

30

31 Preferably, the electrochemical sensor further comprises  
32 a reservoir for storing a second, pre-prepared  
33 electrolyte, flow control means and one or more conduits

1 connected to the electrical cell such that the pre-  
2 prepared electrolyte is used with the electrical cell to  
3 measure the quantity of scale deposited by the test fluid  
4 by measuring the electrical output of the cell as a  
5 function of Reynolds Number.

6  
7 In some examples of the present invention it has been  
8 found that quantitative measurement of the extent of  
9 scaling is more accurately determined by replacing the  
10 test fluid with said pre prepared electrolyte in order to  
11 make measurements.

12  
13 Preferably, the electrolyte is a solution.

14  
15 Preferably, the electrolyte is a solution of brine  
16 containing a suitable tracer.

17  
18 Preferably, the tracer is oxygen.

19  
20 Optionally, the tracer is an ion tracer.

21  
22 Optionally, the tracer is  $Fe(CN)_6^{4-}$ .

23  
24 Preferably, the pre-prepared solution has a saturation  
25 ratio of less than 1.

26  
27 Optionally, the pre-prepared solution has a saturation  
28 ratio of greater than 1.

29  
30 In accordance with a second aspect of the present  
31 invention, there is provided a method of measuring the  
32 scaling properties of a test fluid, the method comprising  
33 the steps of:

1 controlling the velocity of a fluid jet as defined by the  
2 Reynolds number of the fluid when the fluid is in a fluid  
3 flow control means;  
4 releasing the fluid jet from the fluid control means onto  
5 a sensor of an electrochemical cell; and  
6 measuring the electrical output from the sensor as a  
7 function of the Reynolds number of the jet fluid, the  
8 sensor being in contact with a sample of the test fluid.

9  
10 Preferably, the sensor gives a measure of the change in  
11 electrical output as a function of Reynolds number during  
12 use of the fluid flow control means.

13  
14 Preferably, the electrical output provides a measure of  
15 the limiting current response of the electrochemical cell  
16 as a function of Reynolds Number.

17  
18 Preferably, the fluid flow control means is a conduit  
19 having a predefined diameter ( $d$ ) and is positioned at a  
20 height ( $H$ ) above the working electrode or sensor having a  
21 radius ( $r$ ).

22  
23 Preferably, laminar flow of the fluid from the fluid  
24 control means is provided by setting said diameter ( $d$ ),  
25 height ( $H$ ) and radius ( $r$ ).

26  
27 Preferably,  $H/d = 1$ ; and  $r/d < 0.5$ .

28  
29 Preferably, the test fluid has a saturation ratio of  
30 greater than 1.

31 Preferably, the pre-prepared electrolyte is a conductive  
32 Brine solution containing an oxygen tracer.

33

1 Optionally, the method comprises the further step of  
2 isolating the test fluid from a flowing fluid prior to  
3 measuring the electrical output from the electrical cell  
4 as a function of the Reynolds number of the fluid.

5

6 Preferably, the test fluid is isolated by closing valves  
7 arranged upstream and downstream of a predetermined  
8 measuring location in a sample measuring means.

9

10 It has been found that isolation of a sample of the fluid  
11 allows the fluid velocity as defined by the Reynolds  
12 Number to be carefully controlled in the sensor device.

13

14 Preferably the fluid is isolated by removably attaching a  
15 sampling conduit to a first conduit in which the bulk of  
16 the fluid is situated, and by providing valves to isolate  
17 the sampling conduit from the first conduit.

18

19 In accordance with a third aspect of the present  
20 invention there is provided a method of measuring the  
21 scaling properties of a test fluid, the method comprising  
22 the steps of:

23 introducing a jet of test fluid into an electrochemical  
24 cell so as to allow scale to build up on one or more  
25 surfaces in the cell;

26 removing the test fluid from the electrochemical cell;  
27 introducing a pre-prepared solution into the cell; and  
28 measuring the electrical output from the electrochemical  
29 cell.

30

31 Preferably, the test fluid is introduced into the  
32 electrochemical cell at a rate defined by the Reynolds



1 Number of the fluid when contained in a first fluid  
2 control means.

3

4 Preferably, the pre-prepared solution is introduced into  
5 the electrochemical cell at a rate defined by the  
6 Reynolds Number of the fluid when contained in a second  
7 fluid control means.

8

9 Preferably, the electrical output measures the change in  
10 electrical output as a function of Reynolds Number during  
11 use of the fluid flow control means.

12

13 Preferably, the electrical output provides a measure of  
14 the limiting current response of the electrochemical cell  
15 as a function of Reynolds Number.

16

17 Preferably, the fluid flow control means is a conduit  
18 having a predefined diameter (d) and is positioned at a  
19 height (H) above the working electrode or sensor having a  
20 radius (r).

21

22 Preferably, laminar flow of the fluid from the fluid  
23 control means is provided by setting said diameter (d),  
24 height (H) and radius (r).

25

26 Preferably,  $H/d = 1$ ; and  $r/d < 0.5$ .

27

28 Preferably, the pre-prepared solution has a saturation  
29 ratio of less than 1.

30

31 Optionally, the pre-prepared solution has a saturation  
32 ratio of greater than 1.

33



1 In accordance with a fourth aspect of the present  
2 invention, there is provided a computer program for use  
3 with apparatus of the first aspect of the present  
4 invention, and with the method of the second aspect of  
5 the present invention, in which analysis of the  
6 electrical output and the Reynolds number provides  
7 information on the quantity of scale build up and/or the  
8 scaling tendency of the fluid.

9

10 The present invention will now be described by way of  
11 example only, with reference to the accompanying  
12 drawings, in which:

13

14 Figure 1 is a schematic diagram of an embodiment of the  
15 apparatus of the present invention;

16

17 Figure 2 is a graph of the limiting current output of the  
18 electrochemical cell, as measured against the square root  
19 of the Reynolds Number of the jet fluid;

20

21 Figure 3a is a graph of limiting current v Reynolds  
22 number which shows it's variation after scaling has  
23 occurred, figures 3b and 3c illustrate physical changes  
24 to the sensor before and after scaling;

25

26 Figure 4 shows the relationship between the nozzle 12  
27 from which the impinging jet emanates and the sensor 22

28

29 Figure 5 is a schematic representation of the second  
30 embodiment of the present invention, where the  
31 electrochemical cell is positioned in a conduit,  
32 removably connected to a riser;

33

1 Figure 6 shows the limiting current correlation with  
2 scaling index of the water;

3

4 Figure 7 is a schematic diagram of a third embodiment of  
5 the present invention;

6

7 Figure 8 is a graph showing the current response to pre-  
8 prepared brine solutions having different saturation  
9 ratios; and

10

11 Figure 9 is a graph showing the correlation between the  
12 saturation ratio for sample solutions and the slope of  
13 the current similar to that of figure 8.

14

15 Figure 1 shows an electrochemical sensor setup comprising  
16 an electrochemical cell rig 3, having the following  
17 components: The electrochemical cell rig 3 comprises a  
18 sensor (working electrode) 21 position proximate and  
19 normal to the nozzle 9 through which a fluid jet (also  
20 known as an impinging jet) exits from the nozzle 9. In  
21 addition, the cell rig 18 provides support for a  
22 reference electrode (silver-silver electrode) 19 and a  
23 counting electrode 23 made of platinum, in this example.

24

25 The fluid control means consists of a pump 15 positioned  
26 downstream of a needle valve 13 which is used to control  
27 the flow level of the impinging jet fluid. A flow meter  
28 7 is used to measure the amount of flow of the impinging  
29 jet fluid so as to allow calculation of the Reynolds  
30 number of the jet fluid. A nozzle 9 provides the means  
31 by which the impinging jet fluid exits the fluid control  
32 means 5 and contacts the working electrode 21. In this

1 example, a solution tank is provided for storage and  
2 circulation of the impinging jet fluid.

3

4 Figure 2 is a graph of the limiting current  $i_L$  measured  
5 against the square root of Reynolds Number ( $Re^{1/2}$ ). The  
6 graph 41 shows three curves. The first curve illustrates  
7 a situation in which no scale has been deposited upon the  
8 working electrode from the test fluid. Curve 45  
9 illustrates the situation on an unscaled sensor. Curves  
10 46, 47 and 48 illustrate the response from the sensor  
11 with 22%, 39% and 46% of scale coverage respectively  
12 after immersion for 1, 9 and 24 hours in a scaling  
13 solution. These schematic representations show the  
14 difference in the limiting current over the same range of  
15 Reynolds number, where the level of scaling in the sample  
16 is different.

17

| Immersion<br>Time,Hrs | %Scale<br>Coverage |
|-----------------------|--------------------|
| 1                     | 22                 |
| 9                     | 39                 |
| 24                    | 46                 |

18

19 Table 1 shows the resultant scale coverage for different  
20 immersion times.

21

22 In use, the fluid control means or impinging jet system 5  
23 is submerged in a fluid sample, and is used to control  
24 the hydrodynamic regime at the surface of the working  
25 electrode 21. Through analysis of the oxygen tracer  
26 reduction reaction on the sensor surface, the extent of  
27 scaling and the scaling tendency of the fluid can be  
28 determined. In this example the test solution has a  
29 saturation ratio of greater than 1 and is used to deposit

1 scale on the sensor surface. A pre-prepared electrolyte  
2 is used to determine the scale coverage.

3

4 The potential of the electrochemical sensor 1 is applied  
5 to -0.8 volts (with respect to a silver/silver chloride  
6 system) when measurements are started. The impinging jet  
7 system is then controlled through a range of Reynolds  
8 numbers, and the limiting current response is measured as  
9 a function of the Reynolds number. Measuring the  
10 relationship between these two variables, enables scaling  
11 information to be obtained. In this way, the amount of  
12 scale and the scaling tendency of the test fluid can be  
13 determined.

14

15 Figure 6 shows the limiting current correlation with  
16 scaling index (log of saturation ratio) of the test fluid  
17 (water containing electrolyte) for 6000s. The  
18 correlation between the scaling index and the  
19 electrochemical measurement make it possible to measure  
20 the scaling tendency of a fluid.

21

22 Figures 3 a to c and 4 provide more detailed explanation  
23 of a sensor in accordance with the present invention.

24

25 Figure 3a is a graph 2 of limiting current versus  
26 Reynolds Number<sup>1/2</sup> on a sensor. Two curves 4 and 6  
27 illustrate the change in limiting current as a function  
28 of Reynolds number from initial values (curve 4) to final  
29 values (curve 6).

30

31 Figure 3b shows the sensor surface 8 before the use of  
32 the impinging jet which emanates from the nozzle, and  
33 figure 3c shows the sensor surface after this operation.

1 The surface can be seen to be patchy as a result of scale  
2 coverage.

3

4 Limiting current is given as follows:

5 
$$I_{lim} = K Re^{1/2}$$

6

7 The a measure of the scale coverage on the sensor is  
8 given by:

9 
$$\text{Scale coverage} = (K_i - K_f) / K_i$$

10

11 Figure 4 shows the relationship between the nozzle 12  
12 from which the impinging jet emanates and the sensor 22.  
13 The nozzle has an inner diameter d 14 and the nozzle is  
14 placed at a distance H 16 from the sensor 22. Laminar  
15 flow of the surface impinging jet occurs where:

16

17  $H/d = 1$ ; and

18  $r/d < 0.5$ .

19

20 Figure 5 shows a second embodiment of the present  
21 invention, in which the cell rig is installed in the  
22 bypass system of a sub-sea pipeline. The arrows 32 show  
23 the direction of fluid flow through the system. The fluid  
24 flow rate as quantified by calculation of the Reynolds  
25 number is controlled through valves 37, 39 located in the  
26 inlet and outlet of the bypass.

27

28 As shown in Figure 5, the bulk fluid 33 flows down  
29 conduit 31 and a sample (the test fluid) of the bulk  
30 fluid 33 is tapped from the bulk fluid conduit 31 to  
31 measurement conduit or bypass system 35. Once the test  
32 fluid has been tapped, valves 37 and 39 are used to  
33 control the fluid flow rate into the cell 3 where scale

1 is deposited on the working electrode 21. The working  
2 electrode (sensor) 21 is connected to a potentiostat (not  
3 shown)A flow meter (not shown) measures the flow rate. In  
4 this example, to enable measurements of the extent of  
5 scale to be made, the impinging jet is directed onto the  
6 working electrode 21 and the fluid surrounding the sensor  
7 is essentially static.

8  
9 The output current from the electrochemical cell 3 over a  
10 period of time enables the scaling tendency to be  
11 measured. Accordingly, the likelihood and speed with  
12 which scale is likely to precipitate out from the bulk  
13 fluid can be estimated.

14  
15 The ability to operate the electrochemical sensor of the  
16 present invention in situ allows the scaling tendency to  
17 be monitored as the pressure, temperature, water  
18 chemistry and other environmental conditions change. By  
19 locating the apparatus of the present invention within  
20 the precise zone of interest within a pipeline, the  
21 present invention can monitor the scaling tendency from  
22 individual branches of a pipe in, for example, a  
23 horizontal well which goes into the main pipeline.  
24 Information feedback from the well can provide an early  
25 indication of scaling potential problems. Hence, the  
26 present invention enables the operator to manage and  
27 selectively control individual wells and to inject the  
28 correct amount of scale inhibitor in these wells.

29  
30 Further advantageously, the present invention can detect  
31 small amounts of scale and can rapidly (within a matter  
32 of 30 minutes or so) determine the scaling tendency of  
33 the sample. As a consequence, the operator of the



1 conduit, whether it be a riser from an oil well, a subsea  
2 pipeline, a pipe in a desalination plant, or otherwise,  
3 can quickly determine the scaling tendency in these  
4 positions and can anticipate problems associated with the  
5 build up of scale.

6  
7 In use, the apparatus of the present invention will be  
8 connected to an operator terminal by means of a suitable  
9 telemetry system. This will allow data to be collected  
10 frequently by the operator using a communications  
11 protocol. Real-time data from the oil well or other  
12 location will be sent to a PC based surface system that  
13 monitors this location. In addition, multiple systems  
14 can be used at varying locations in a pipeline system or  
15 well or the like, and all of these individual systems can  
16 feed data back to a single PC for analysis by the  
17 operator, who may then use this data to determine it is  
18 necessary to add chemical scale inhibitors to that  
19 location, or to otherwise remove or limit the scale  
20 measured at that location.

21  
22 Figure 7 shows a further embodiment of the present  
23 invention similar to that shown in Figure 7. Figure 7 is  
24 an embodiment of the invention in which a pre-prepared  
25 solution is used when measuring the scale coverage of a  
26 working electrode. The sensor arrangement 51 has two  
27 fluid flow paths 53 and 55.

28  
29 Flow path 53 is similar to the flow path shown in figure  
30 7 and allows a fluid sample to be taken from a pipe 57  
31 and fed through an electrochemical cell 61 via a conduit  
32 59. Flow path 55 includes a solution tank 63 and a pump  
33 69 which allow the supply of a pre-prepared electrolyte



1 (brine in this example) to the electrochemical cell rig.  
2 It has been found that the use of this electrolyte allows  
3 a more accurate measure of the scale coverage to be  
4 achieved as the electrolyte is pre-prepared and  
5 substantially free from the contaminants that are often  
6 found in the bulk fluid contained in the pipeline 57.

7  
8 A potentiostat 65 is used to measure the electrical  
9 output of the electrochemical cell and this is connected  
10 to a personal computer or network 69 by means of a  
11 suitable connection. This allows the end user to monitor  
12 the scale coverage or scaling tendency from an office or  
13 lab.

14  
15 In order to measure scale coverage using this example of  
16 the present invention, test fluid from the pipeline 57 is  
17 fed into the electrochemical cell 61 via the conduit 59  
18 and the control valve 58 such that the test fluid  
19 continuously impinges upon the sensor surface 62. Valves  
20 58 and 60 are used to control the rate at which the which  
21 test fluid enters the cell, the flow is measured by a  
22 flow meter (not shown) from which the Reynolds number can  
23 be calculated. At this stage, the electrical output of  
24 the cell 61 is not measured however, as the rate of test  
25 fluid entry into the cell is a variable in the system, it  
26 is desirable to control and measure this variable as it  
27 shows the extent to which the flow is laminar or  
28 turbulent. The test fluid flow is controlled so that it  
29 continuously impinges upon the sensor surface 62 (working  
30 electrode) for a predetermined period of time and scale  
31 is deposited onto the sensor surface 62.

32

1 The extent of scale on the surface 62 is measured using  
2 the pre-prepared electrolyte (typically an electrolytic  
3 solution such as brine) and is provided to the cell 61  
4 via flow path 55. The brine solution is pumped  
5 continuously through the cell 61 in a controlled manner  
6 such that the Reynolds Number of the flowing brine can be  
7 measured. The scale coverage of the sensor 62 is  
8 measured using the potentiostat 65 to record the output  
9 current of the cell 61.

10

11 In this example of the present invention, the scaling  
12 tendency of the test fluid is measured as follows. Test  
13 fluid from the pipeline 57 is fed into the  
14 electrochemical cell 61 via the conduit 59 and the  
15 control valve 58 such that the test fluid continuously  
16 impinges upon the sensor surface 62. Valves 58 and 60 are  
17 used to control the rate at which the test fluid enters  
18 the cell. The Reynolds Number can therefore be  
19 calculated.

20

21 The current output of the cell 61 is measured as a  
22 function of time and the scaling tendency can be  
23 calculated and provided to a user through the PC or  
24 network 69.

25

26 Figure 8 is a graph 73 showing the current response  
27 (current density) as a function of time for electrolytic  
28 solutions (brine) having different saturation ratios.  
29 The saturation ratios for curves 75, 77, 79 and 81 are  
30 17.8, 8.91, 0.27 and 1.09 respectively. Curve 79 has a  
31 negative gradient.

32

1 Figure 9 is a graph 83 which illustrates the correlation  
2 between saturation ratio and the slope of the current  
3 values against time as exemplified in figure 8.  
4 Curve 85 shows that scaling of the fluid does not occur  
5 in region 89 where the saturation ratio is below  
6 approximately 1 and scaling does occur in region 87 of  
7 the graph 83 where the scaling ratio is above  
8 approximately 1. This region is where the fluid is  
9 supersaturated.

10

11 The present invention has a number of advantages over the  
12 known prior art. In particular, the present invention  
13 allows early measurement of scale or other particulates,  
14 and provides a means by which the scaling tendency of the  
15 fluid in question can be measured. Measurement of the  
16 scaling tendency, as well as the bulk amount of scale,  
17 allows the operator to predict the amount of inhibitor  
18 that should be used, and also to predict when in the  
19 future this inhibitor should be applied.

20 Improvements and modifications may be incorporated  
21 herein, without deviating from the scope of the  
22 invention.